

Ring-closing-opening Copolymerization of Phthalaldehyde and Epoxide towards Acid-degradable Polyether and Polyurethane

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Abstract Incorporation of acetal groups in the backbone is a potent strategy to create polymers that are cleavable or degradable under acidic conditions. We report here an in-depth study on the ring-closing-opening copolymerization of *o*-phthalaldehyde (OPA) and epoxide using Lewis pair type two-component organocatalysts for producing acetal-functionalized polyether and polyurethane. Notably, triethylborane as the Lewis acid, in comparison with tri(*n*-butyl)borane, more effectively enhances the polymerization activity by mitigating borane-induced reduction of the aldehyde group into extra initiating (borinic ester) species. Density functional theory (DFT) calculations present comparable energy barriers of OPA-epoxide cross-propagation and epoxide self-propagation, which is consistent with the experimental finding that an alternating-rich copolymer comprising mostly OPA-epoxide units but also epoxide-epoxide linkages is produced. In particular, when epoxide is added in a large excess, the product becomes a polyether containing acetal functionalities in the central part of the backbone and thus being convertible into polyurethane with refined acid degradability.

Keywords Degradable polymer; Polyurethane; Polyether; Anionic polymerization; Ring-opening polymerization

Citation: Pang, J.; Zhou, Y. B.; Liu, L. J.; Zhang, H. X.; Zhao, J. P. Ring-closing-opening copolymerization of phthalaldehyde and epoxide towards acid-degradable polyether and polyurethane. *Chinese J. Polym. Sci.* 2025, 43, 964–972.

INTRODUCTION

Polyurethane (PU) is a versatile polymeric material, with global production exceeding 24 million tons since 2018 and growing at an annual rate of 4%.^[1,2] In both industry and laboratories, PUs are mostly synthesized by the step-growth polymerization of diisocyanates and polyether/polyester polyols with diols, diamines, and other additives,^[3,4] though efforts have been made to develop non-isocyanate pathways.^[5,6] The massive production and ubiquitous use of PUs has brought their recycling to the research frontier.^[7,8] The susceptibility of polyester-based PUs to degradation/depolymerization under pyrolytic, acidic, alkaline, or enzymatic conditions is frequently documented and utilized for PU recycling.^[9–12] In sharp contrast, most polyether-based PUs are much more resistant to degradation because of the chemical stability of the polyether segments, as well as the carbamate and urea moieties. To address this challenge, cleavable groups, such as esters, carbonates, acetals, and imines, *etc.*, have been incorporated into polyether backbones by copolymerization of epoxides, the main constituent monomers, and

other types of monomers.^[13,14] However, this approach cannot ensure that each polyether segment contains the same number of cleavable groups at the same positions, thus leading to irregular degradation of PU and complex products that may hamper effective recycling.

Owing to their easy cleavage under mildly acidic conditions, acetal groups have received widespread attention for the construction of acid-degradable polymers.^[15–20] The strongly polarized carbon-oxygen double bond enables the homopolymerization of aldehydes into polyacetals through either a cationic or anionic approach.^[21–23] Since its first report by Aso in 1967^[24], *o*-phthalaldehyde (OPA) has received special attention because of its unique ring-closing polymerization into poly(cyclic)acetal (POPA). At temperatures above –43 °C, POPA undergoes depolymerization because of the poor thermodynamic stability of the cyclic hemiacetal end group.^[25] It is therefore essential to terminate the polymerization by *e.g.* an anhydride to ensure the room-temperature stability of POPA. Notably, end-capping of POPA with a stimuli-responsive group was conducted to obtain self-immolative polymers.^[26,27] Copolymerization of two or more aldehydes has been shown to be a valid method for the synthesis of stable polyacetals, as exemplified by the copolymerization of OPA with substituted benzaldehyde,^[28] butyraldehyde,^[29,30] and acetaldehyde ethylglyoxal.^[31] An alternative approach is to copolymerize OPA with structurally distinct (vinyl)

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Special Topic: Depolymerizable Polymers

Received December 18, 2024; Accepted January 17, 2025; Published online March 4, 2025

monomers.^[32–37]

Epoxides constitute a family of versatile raw materials for polymer synthesis *via* ring-opening (co)polymerization. In particular, an increasingly rich variety of degradable polyesters and polycarbonates has been created in recent decades by the copolymerization of epoxides with carbon dioxide,^[38,39] cyclic anhydride,^[40,41] aromatic lactones,^[42–44] iso(thio)cyanates,^[45,46] etc.^[47,48] Typically, the non-homopolymerizability and superior electrophilicity of these compounds allow copolymerization to occur in a highly or even exclusively alternating manner. Among the numerous catalysts/initiators employed, phosphazene bases (PBs), a class of organobases featuring low nucleophilicity and tunable basicity, have shown special potency to fulfill living/controlled epoxide-based copolymerization.^[49,50] Addition of an appropriate amount of Et₃B to form a Lewis pair catalyst significantly enhances the copolymerization efficiency by activating the epoxide.^[51,52]

Recently, anionic copolymerization of OPA and epoxides has been shown to occur at room temperature, initiated/catalyzed by a tetrabutylammonium chloride salt and Et₃B. The products exhibited much better thermal stability than POPA and good acid-degradability due to the acetal-ether type backbones.^[53] In addition, sequence-controlled copolymerization of OPA with cyclic anhydride or terpolymerization with epoxides and carbon dioxide has recently been achieved, distinguishing OPA as a versatile feedstock for enriching the catalog of acetal-based polymers with degradability and/or recyclability.^[54,55] To shed more light on the mechanism and versatility of OPA-epoxide copolymerization, we report an in-depth study using 1,4-benzenedimethanol (BDM) as the initiator and PB-Et₃B as the catalyst, revealing the im-

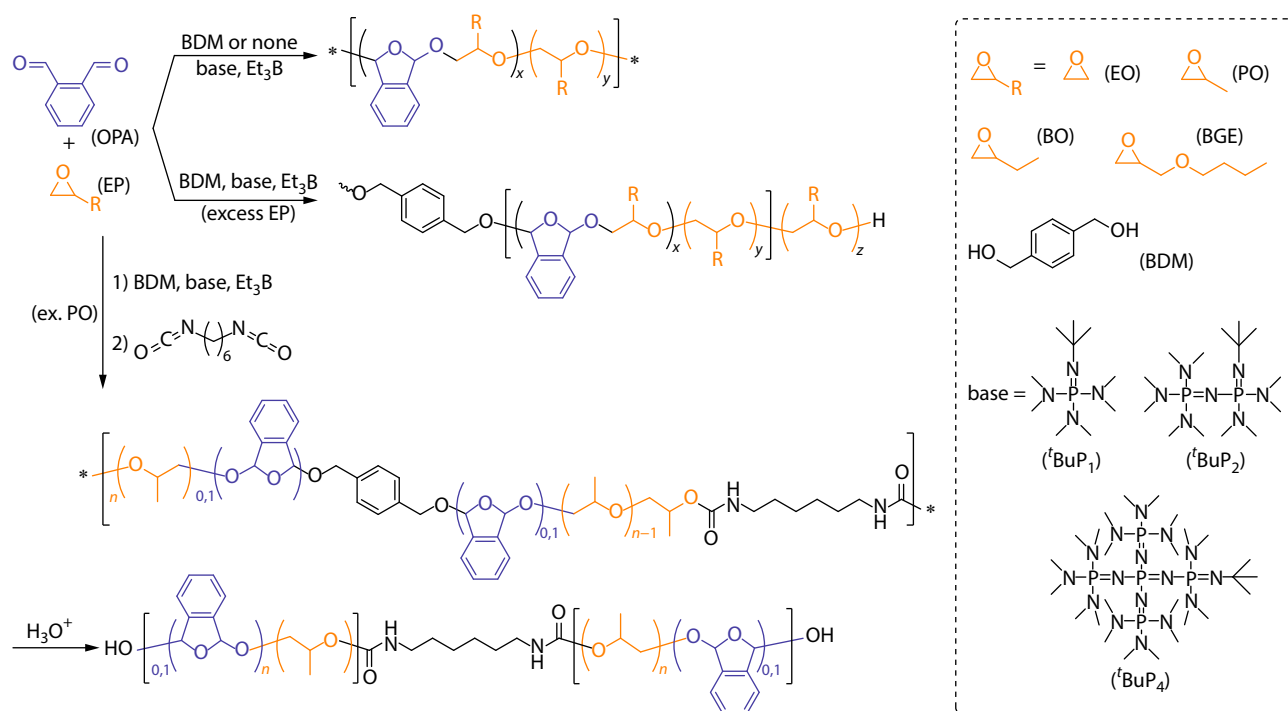
pacts of the structure, loading, and feeding order of the catalytic components, and disclose the potential of some of the products, *i.e.* the acetal-functionalized polyethers, in constructing acid-degradable PU (Scheme 1).

EXPERIMENTAL

The experimental section, complementary data, and DFT calculation details are presented in the electronic supplementary information (ESI).

RESULTS AND DISCUSSION

It was first shown that ^tBuP₂ alone is inactive for catalyzing the copolymerization of OPA and propylene oxide (PO) added in an equal molar amount with a target degree of polymerization (*D_p*) of 40 (OPAPO-1 in Table 1). When Et₃B was used in 3 equiv. of ^tBuP₂, the viscosity of the reaction mixture evidently increased after 24 h, implying polymer formation (OPAPO-2 in Table 1). A (near) unimodal and narrow molar mass distribution (*D*=1.16; Fig. 1A) was determined by size exclusion chromatography (SEC), although the apparent number-average molar mass (*M_{n,SEC}*, 5.5 kg·mol^{−1}) was lower than the theoretical molar mass calculated from the monomer-to-initiator feed ratio (*M_{n,th}*). Nuclear magnetic resonance (NMR) spectra showed the disappearance of the aldehyde and epoxy groups and the emergence of the acetal methine (–OCHO–) and ether methine/methylene (–OCH₂CH(CH₃)O–) groups derived from OPA and PO (Fig. 1B and Fig. S1 in ESI), respectively, concomitant with full consumption of OPA and PO. Given that OPA is unable to homopolymerize under such a condition, and that the NMR spectra are distinct from those of POPA and poly(propylene oxide) (PPO), it is likely that the two monomers copolymerize in an alternating



Scheme 1 General reaction scheme for OPA-epoxide copolymerization, construction and acid-degradation of acetal-functionalized polyether-PU.

Table 1 Conditions and results of the copolymerization of OPA and epoxides. ^a

Entry	PB	[OPA] ₀ /[epoxide] ₀ / [OH] ₀ /[PB] ₀ /[Et ₃ B] ₀ ^b	Time (h)	Conv. (%)		<i>M</i> _{n,th} ^d (kg·mol ⁻¹)	<i>M</i> _{n,SEC} ^e (kg·mol ⁻¹)	<i>Đ</i> ^e
				OPA ^c	EP ^c			
OPAPO-1	^t BuP ₂	20/20/1/0.1/0	24	0	0	7.8	/	/
OPAPO-2	^t BuP ₂	20/20/1/0.1/0.3	24	100	100	7.8	5.5	1.16
OPAE0	^t BuP ₁	20/20/1/0.1/0.3	16	86	100	7.1	4.7	1.12
OPABO	^t BuP ₂	20/20/1/0.1/0.3	48	96	83	8.3	4.1	1.24
OPABGE	^t BuP ₂	50/50/1/0.25/0.75	24	100	100	24.8	7.1	1.30
OPAPO-3(1) ^f	^t BuP ₂	20/20/0.04/0.1/0.3	50	>99	100	96.0	38.3 (47.7%); 16.5 (52.3%)	1.04; 1.12
OPAPO-3(2) ^g	^t BuP ₂	20/20/0.04/0.1/0.3	50	>99	100	96.0	24.5 (40.7%); 11.2 (59.3%)	1.04; 1.08
OPAPO-4	^t BuP ₁	20/20/0.04/0.1/0.3	62	92	79.4	96.0	18.4 (28.9%); 6.6 (71.1%)	1.04; 1.20
OPAPO-5	^t BuP ₄	20/20/0.04/0.1/0.3	18	93	100	96.0	31.0 (40.7%); 14.0 (59.3%)	1.04; 1.09
OPAPO-6 ^h	^t BuP ₂	20/20/1/0.1/0.3	24	100	100	7.8	2.1	1.22
OPAPO-7	^t BuP ₁	20/20/0/0.1/0.3	96	>99	91.6	/	8.9	1.25
OPAPO-8	^t BuP ₁	20/20/0/0.1/1.5	22	100	100	/	6.2	1.23
PO-co-OPA-1	^t BuP ₂	25/125/1/0.25/1.5	30	100	96	21.3	13.2 (66.5%); 6.1 (33.5%)	1.04; 1.07
PO-co-OPA-2	^t BuP ₂	3/50/1/0.025/0.075	24	93	>99	6.8	8.9	1.09
EO-co-OPA	^t BuP ₂	3/50/1/0.025/0.075	2	100	100	5.3	6.5	1.06
PO-co-OPA-3 ⁱ	^t BuP ₁	1/20/1/0.025/0.075	48	100	87	2.4	3.2	1.06
			72				36.5	1.89

^a Conducted at 25 °C in THF using BDM as the initiator, except for OPAPO-7 and OPAPO-8 which were performed without an exteriorly added initiator; ^b Molar feed ratio of OPA, epoxide, hydroxyl group of BDM, PB, and Et₃B; ^c Conversion of OPA and epoxide determined by ¹H-NMR analysis; ^d Theoretical number-average molar mass calculated by the feed ratio and monomer conversion; ^e Number-average molar mass and molar mass distribution obtained from SEC analysis (THF, 35 °C, PS standards); ^f Feeding order: OPA, PO, BDM, PB, Et₃B (also for other entries except the next); ^g Feeding order: OPA, PO, BDM, Et₃B, PB; ^h With diethylmethoxyborane added in 0.25 equiv.; ⁱ With HDI added in a near-equal molar amount as BDM after 48 h of the copolymerization and reacted for another 24 h to form the polyether-PU.

manner.^[26,52,53] However, integral of the acetal-adjacent methine in the PO-OPA diad (4.24–3.84 ppm) was less than half of the rest of the ether signals (3.84–3.13 ppm) in the ¹H-NMR spectrum. Matrix-assisted laser desorption/ionization time-of-flight mass spectrometry (MALDI-TOF MS) also suggested that the copolymer is not exclusively constituted by PO-OPA units and that PO-PO-type linkages coexist (Figs. 1C and 1D). Hence, the self-propagation of the PO is indicated. Nevertheless, the copolymer shows a much better thermal stability (decomposition temperature is more than 315 °C) than POPA and a much higher glass transition temperature (*T*_g = 54.7 °C) than PPO (Fig. S2 in ESI), indicating that it is compositionally distinct from the homopolymers, so that an alternating-rich structure can be inferred. The same reaction conditions were then applied to 1,2-butylene oxide and *n*-butyl glycidyl ether, while a milder PB (^tBuP₁, Scheme 1) was used in the catalytic system for ethylene oxide (EO) because of its greater activity (OPAE0, OPABO, and OPABGE in Table 1). The characterization data (Figs. S3–S7 in ESI) confirmed the occurrence of ring-closing-opening copolymerization and the formation of acetal-ether type and alternating-rich copolymers, as well as epoxide-epoxide linkages.

DFT calculations were conducted using simplified models to elucidate the copolymerization mechanism (Fig. 2). The base-deprotonated and Et₃B-coordinated alkoxide species (**IN1**) reacts with Et₃B-activated OPA to form a thermodynamically unfavored intermediate (**IN2**) via an energy barrier (**TS1**) of 18.9 kcal·mol⁻¹. **IN2** then promptly produces a cyclic acetal-semiacetal species (**IN3**) by intramolecular nucleophilic attack with an exceedingly low energy barrier of 13.4 kcal·mol⁻¹

(**TS2**). Apparently, the ring-closing of OPA (transformation from **IN1** to **IN3**) is a rapid process, but the deprotonated semiacetal species is thermodynamically unstable, even though it is coordinated with Et₃B. It is until **IN3** attacks Et₃B-activated EO that a stable ring-opened product (**P1**) is generated (Gibbs free energy decreases by –6.4 kcal·mol⁻¹). A relatively high energy barrier (**TS3**, 25.7 kcal·mol⁻¹) needs to be surmounted, which then becomes the overall barrier of the cross-propagation (formation of the OPA-EO alternating unit). Notably, **TS3** contains a high degree of freedom, and the optimized structure may not correspond to the lowest barrier in the potential surface. However, the contribution of other structures to the free energy is not considered; therefore, the actual energy barrier may be easier to overcome than the calculated one. On the other hand, direct ring-opening of EO by **IN1** to generate an EO-EO diad (**P2**) needs to overcome an energy barrier of 21.8 kcal·mol⁻¹ (**TS1'**), which is consistent with the competitiveness of the epoxide self-propagation experimentally observed above.

The next few experiments were designed to investigate the molar mass control; in particular, the discrepancy between *M*_{n,SEC} and *M*_{n,th} OPAPO-3(1) and OPAPO-3(2) were performed with the target *D*_p increased to 1000 (Table 1), and the catalysts were added in different ways. For OPAPO-3(1), OPA, PO, BDM, ^tBuP₂, and Et₃B were loaded successively as described above. For OPAPO-3(2), ^tBuP₂ was added. Full conversion of the monomers was achieved in 50 h. The bimodal molar mass distribution is shown in both cases (Fig. S8 in ESI), indicating the existence of an extra monofunctional initiator apart from

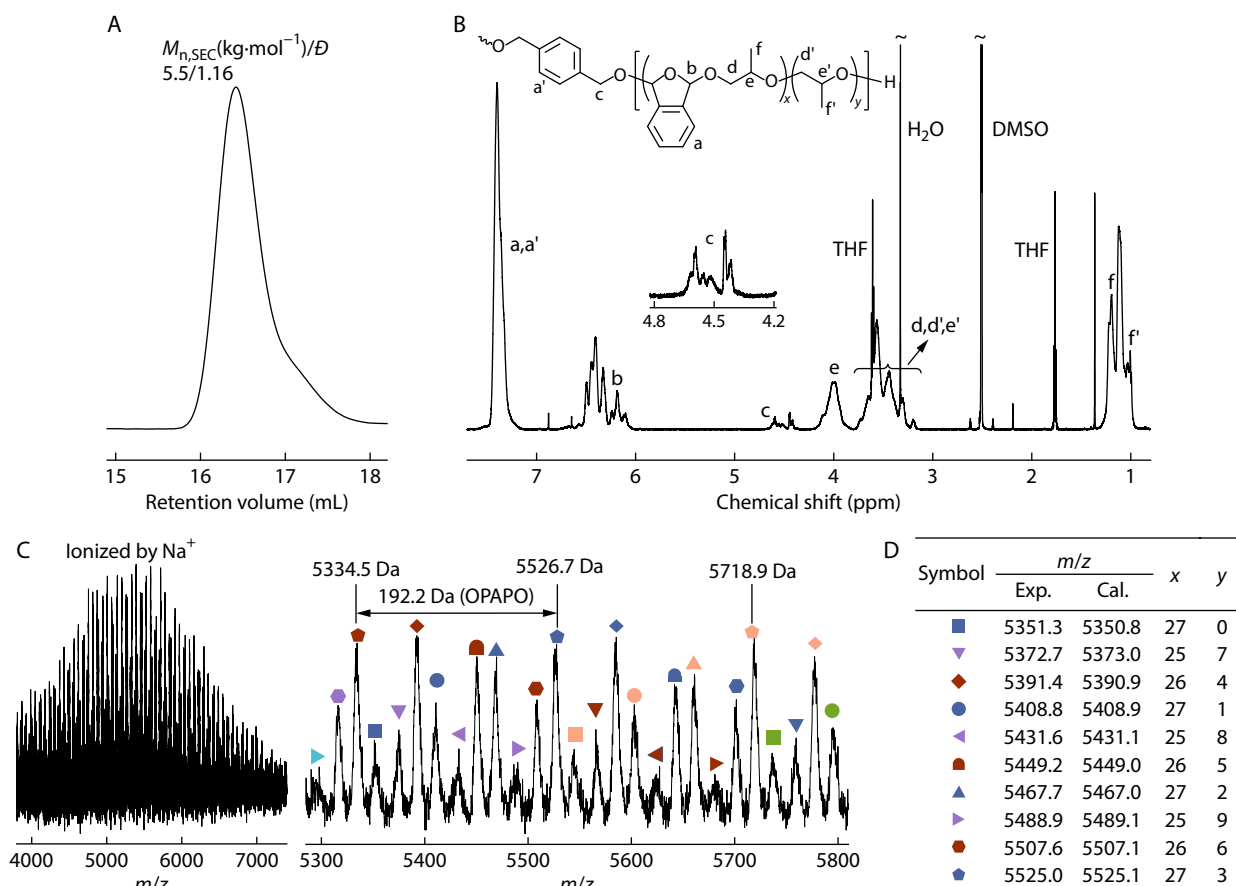


Fig. 1 SEC trace (A; THF, 35 °C), ^1H -NMR spectrum (B; in $\text{DMSO}-d_6$), and MALDI-TOF mass spectrum (C) with an information table of selected peaks (D) of the product of entry OPAPO-2 in Table 1.

the difunctional BDM. Notably, the fraction of the lower-molar-mass population was distinctly higher in the case of OPAPO-3(2), indicating that the amount of monofunctional initiator increased when $^t\text{BuP}_2$ was added later than Et_3B . In other words, a side reaction occurs on the other components to generate the monofunctional initiator, which can be mitigated by $^t\text{BuP}_2$.

The copolymerization of OPA and PO catalyzed by $^t\text{BuP}_1$ - Et_3B and $^t\text{BuP}_4$ - Et_3B , respectively, was carried out under the same conditions as OPAPO-3(1) (OPAPO-4 and OPAPO-5 in Table 1). The use of $^t\text{BuP}_1$ resulted in a higher fraction of lower-molar-mass population in comparison with $^t\text{BuP}_2$, indicating that the side reaction is slightly more pronounced when the basicity is lower. However, despite the high basicity of $^t\text{BuP}_4$, the side reaction was remarkably more intensive, as indicated by the massive lower-molar-mass population in the SEC. It then seems that the bulkiness of $^t\text{BuP}_4$ causes its poor ability to suppress side reactions. In conjunction with the fact that OPA is not homopolymerizable but can be fully consumed even though the epoxide, added in an equal molar amount, is partly consumed in its self-propagation, it can be inferred that the “missing” part of OPA is consumed in this side reaction that produces the monofunctional initiator (or chain transfer agent).

In the 1970s, Mikhailov *et al.* reported that trialkylboranes could reduce aromatic aldehydes to benzyl alcohols (through

borinic ester species).^[56] Here, we employed tri(*n*-butyl)borane ($^n\text{Bu}_3\text{B}$) for comparison with Et_3B . ^1H -NMR tests showed that both Et_3B and $^n\text{Bu}_3\text{B}$ reacted with OPA to form boronic esters and alkenes (Fig. 3). Nevertheless, the conversion of $^n\text{Bu}_3\text{B}$ was significantly higher than that of Et_3B (comparison of signals *b* and *b'*, *i* and *i'* in Fig. 3). This can be attributed to easier hydride transfer on the secondary β -carbon (methylene versus methyl), which also explains the inactivity shown by other Lewis acids including triisobutylborane and triethylaluminum, *etc.* for OPA-epoxide copolymerization.^[53]

Diethylmethoxyborane (Et_2BOME) was then introduced to explicitly reveal the effect of the borinic ester (OPAPO-6 in Table 1). SEC showed a significantly lower molar mass (in comparison with OPAPO-2) with a distinct bimodal distribution, and the MALDI-TOF mass spectrum presented both BDM- and methoxy-initiated species (Fig. S9 in ESI), corroborating the role of the borinic ester as an extra initiator or chain-transfer agent. When the copolymerization is performed without an externally added initiator (OPAPO-7 in Table 1), the conversion of PO remains incomplete in 96 h while OPA is fully consumed, indicating that OPA participates in reactions other than copolymerization. A similar experiment was conducted with five Et_3B additions (OPAPO-8 in Table 1), which resulted in full consumption of both monomers in a much shorter time, although the measured molar mass was lower, indicating a higher number of initiat-

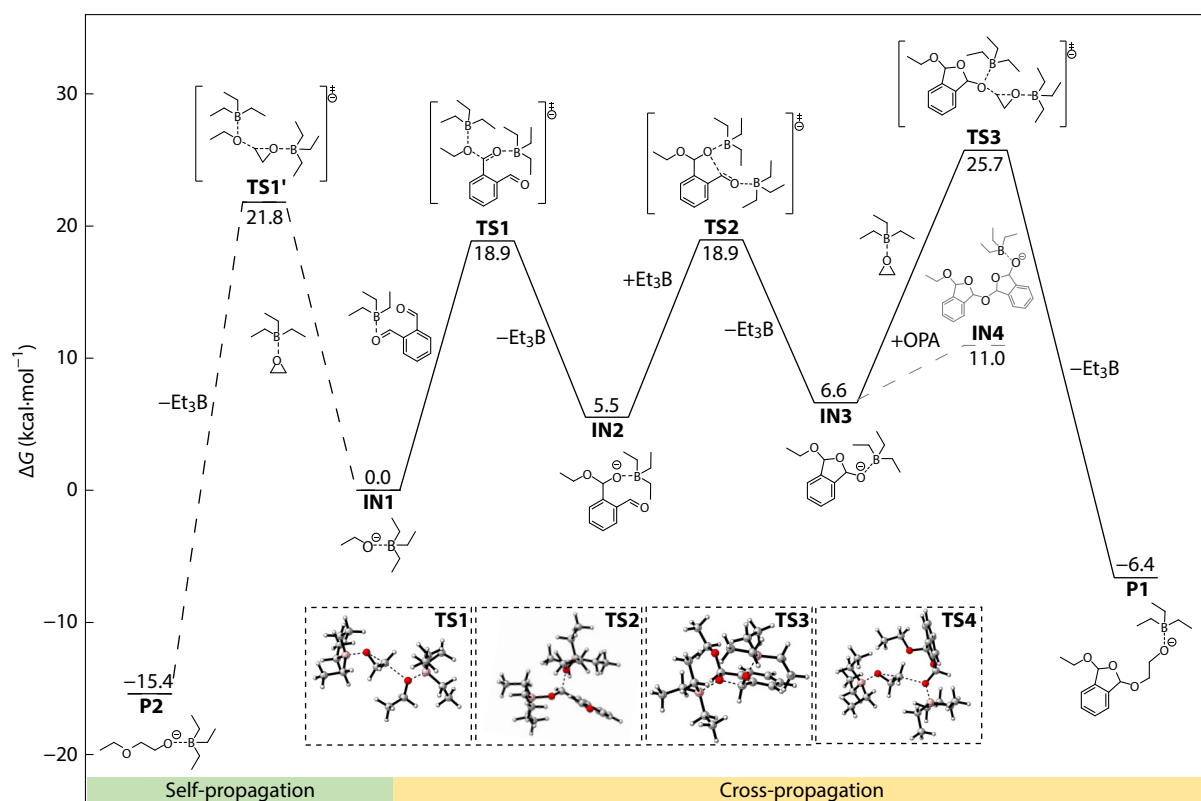


Fig. 2 Energy profile for the copolymerization of OPA and EO by DFT calculations.

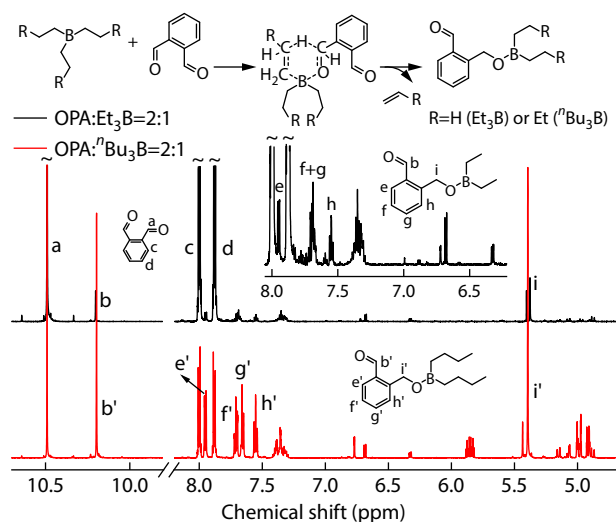


Fig. 3 Upper: reaction between the acetal group of OPA and trialkylboranes. Lower: ^1H -NMR spectra (in $\text{DMSO}-d_6$) of the mixture of OPA and $\text{Et}_3\text{B}/i\text{Bu}_3\text{B}$ in a molar ratio of 2/1.

ing/chain-transfer species. ¹H-NMR and MALDI-TOF MS analyses showed that the obtained copolymers ended with an OPA-derived benzyloxy group (Figs. S10 and S11 in ESI), thus confirming the *in situ* generation of the borinic ester by the Et₃B-reduction of OPA and chain growth therefrom.

The acetal groups in the backbone enabled the OPA-PO copolymer to degrade easily under acidic conditions, although they contained PO-PO linkages. When treated with HCl (0.15 mol/L, *ca.* 0.5 equiv. of the acetal group) in a

THF/water (ca. 1/10 V/V) mixed solvent, the product of OPA-PO-2 showed a rapid decrease in molar mass, with the SEC peak of the copolymer disappearing completely in 30 min (Fig. S12a in ESI). ¹H-NMR spectrum indicated that the degradation product mainly consisted of small-molecule aldehydes and cyclic acetals. The aldehyde groups were predominantly derived from OPA, while mono-benzaldehyde was also present (6.7 ppm), indicating that approximately half of the aldehyde groups underwent cycloacetalization with 1,2-propanediol derived from the PO units (Fig. S12b in ESI).^[53] The chemical shifts of the ether methylene and methine groups at δ =3.2–3.5 ppm and the methyl groups at δ =1.2 ppm indicate the presence of the diol type PO-PO dimer, derived from the PO-PO linkages in the copolymer, while longer diols are not discernable. Thus, the degradation product further confirms the formation of an alternating-rich OPA-PO copolymer with PO-PO linkages as minor components. *In situ* ATR-IR characterization showed that degradation was completed within 1 h, during which the absorption of the acetal group centered at 963 cm⁻¹ gradually decreased. Concurrently, the absorption centered at 1700 cm⁻¹ gradually increased, indicating the recovery of the carbonyl groups (Figs. S12c and S12d in ESI).

Inspired by the concurrence of cross- and self-propagation of epoxides, as well as the exceeding activity of OPA towards the reaction with alkoxide species, we are inspired to use OPA-epoxide copolymerization to create acetal-functionalized polyethers with epoxide added in large excesses. PO-co-OPA-1 (Table 1) was prepared by adding PO to 5 equiv. of OPA. A relatively high quantity of Et_3B was used to compen-

sate for the possible loss in the OPA reduction to ensure the complete consumption of PO, and the reaction was monitored by *in situ* ATR-IR spectroscopy (Fig. 4). In the first stage, the absorption at 828 cm^{-1} (stretching of PO) decreased, accompanied by an increase in the absorption at $1160\text{--}1020\text{ cm}^{-1}$ (stretching of the open-form C–O–C), which corresponds to the ring-opening of PO (Fig. 4). Concurrently, the absorption at 1700 cm^{-1} (stretching of the OPA carbonyl group) gradually diminished, together with an increase in the absorption at $980\text{--}940\text{ cm}^{-1}$ (out-of-plane bending of 1,2-substituted benzene), corresponding to the conversion of aldehyde to acetal. At approximately 2.5 h, the absorptions

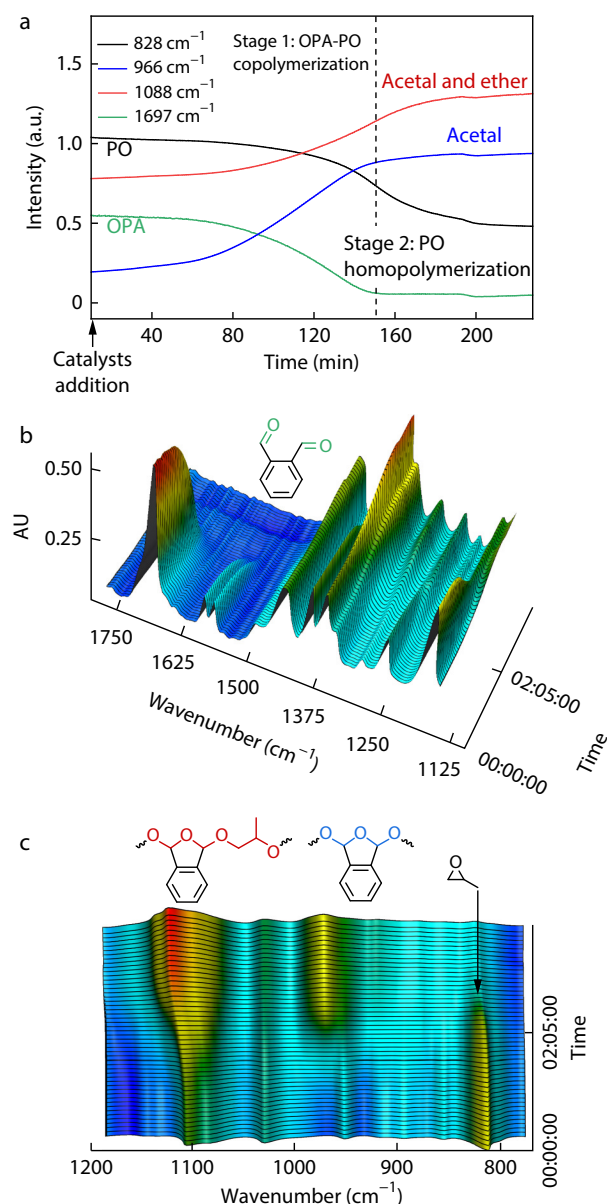


Fig. 4 *In situ* ATR-IR results of the copolymerization of OPA and PO (PO-co-OPA-1 in Table 1). (a) Evolution of the intensities of characteristic IR absorption bands at 828 , 966 , 1088 , and 1697 cm^{-1} . (b) Stacked *in situ* ATR-IR spectra of the aldehyde region. (c) Stacked *in situ* ATR-IR spectra of the acetal and ether region.

related to OPA and acetal stopped changing, while the conversion of PO into polyether continued into the second stage. Clearly, OPA and PO copolymerize first, most likely in an alternating-rich manner, to produce acetal-containing segments. Once OPA was used, the remaining PO underwent homopolymerization to form acetal-free (PPO) segments.

Because PO-co-OPA-1 still resulted in a bimodal molar mass distribution, we further reduced the OPA-to-PO ratio to 3/50 and used a much lower catalyst loading (PO-co-OPA-2 in Table 1). Thus, the Et_3B -OPA side reaction was substantially suppressed, as indicated by the near unimodal SEC peak (Fig. S13 in ESI). The coexistence of OPA and PO units, *i.e.* formation of an acetal-functionalized α,ω -dihydroxy PPO, is corroborated by the MALDI-TOF mass spectrum (Fig. S14 in ESI). The product afforded by acidic hydrolysis was shown to comprise mainly OPA-free PPO diols by MALDI-TOF MS (Fig. S15 in ESI). PPO chains with a chloride end group were also present as a minor population, indicating the occurrence of chain-end chlorination by HCl during degradation. Importantly, acidic hydrolysis results in a halved molar mass, and the initiator (BDM) moiety is not tethered to the majority of the PPO chains, which clearly demonstrates that OPA is enchain in the very early stages of the copolymerization though added in a small quantity owing to its much higher electrophilicity than PO (Fig. 2); thus, the acid-cleavable acetal groups are enriched in the central parts of the polyether chains. Similarly, OPA-EO copolymerization with EO added in large excess yields a backbone acetal-functionalized PEO with unimodal and narrow molar mass distribution (EO-co-OPA in Table 1; Figs. S16 and S17 in ESI). The MALDI-TOF mass spectrum of the acidic hydrolysis product presented only PEO diols free of chloride and BDM groups (Fig. S18 in ESI).

The α,ω -dihydroxy- and acetal-functionalized characteristics of the OPA-PO copolymer pave the way for acid-degradable polyether-PU.^[57] PO-co-OPA-3 (Table 1) was performed with OPA and PO added to 1 and 20 equiv. for the BDM hydroxyl groups. After 48 h, a high conversion of PO was achieved when hexamethylene diisocyanate (HDI) was introduced into 1 equiv. of BDM. After 24 h, the reaction mixture became highly viscous, indicating the occurrence of step-growth polymerization and the formation of PU, which was verified by SEC and ^1H -NMR (Figs. 5A and 5B). Treating PU in a tetrahydrofuran (THF) solution with aqueous HCl (0.15 mol/L) for 12 h resulted in a drastic decrease in molar mass. The product showed a bimodal distribution in SEC. The major population has a molar mass very close to that of the original polyether, conforming to the expected degradation product formed after cleavage of the acetal groups, *i.e.* separated PPO chains, each containing two carbamate groups in the center (PPO-HDI-PPO). The MALDI-TOF mass spectrum confirmed the existence of carbamate groups (hard segments of PU) in the degradation product (Figs. 5C and 5D). The minor (higher-molar-mass) population observed in SEC is most probably due to the lack of OPA units on one or both sides of some of the original PPO chains, resulting from the use of a very small amount of OPA, causing incomplete separation of adjacent soft segments. Chain-end chlorination became much more

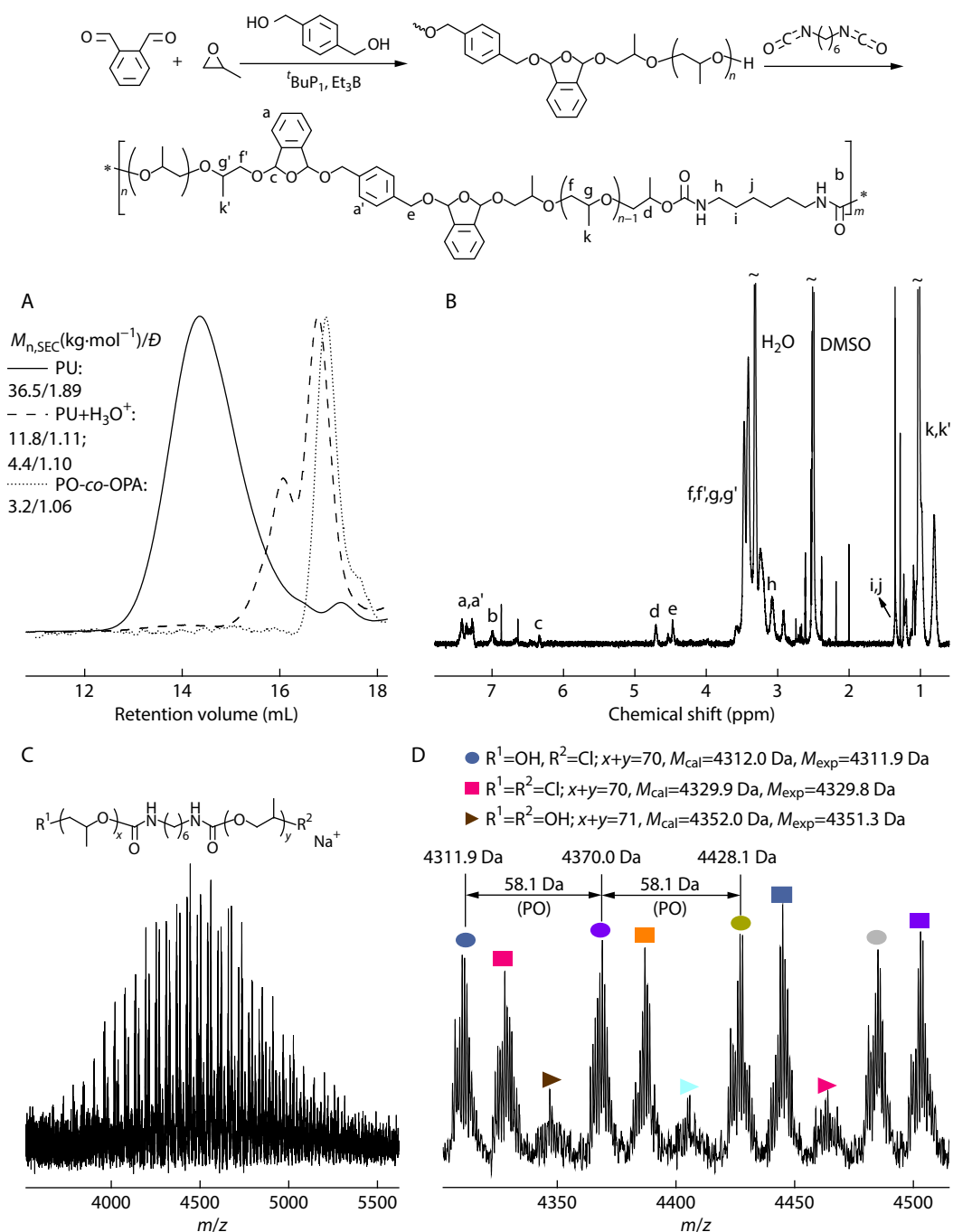


Fig. 5 Results of acetal-functionalized PU. (A) SEC traces (THF, 35 °C) of the original polyether diol (product of PO-co-OPA-3 in Table 1), PU, and the degradation product. (B) ¹H-NMR spectrum of PU (in DMSO-d₆). (C, D) MALDI-TOF mass spectrum (reflective mode, ionized by Na⁺) of the degradation product of PU.

pronounced, perhaps because of the higher HCl-to-acetal ratio and/or much longer degradation time.

CONCLUSIONS

The ring-closing-opening copolymerization of OPA and epoxide occurs from a hydroxy initiator with the aid of a Lewis pair-type two-component organocatalytic system. It is important to reveal that some of the OPA aldehyde groups are reduced by the Lewis acidic trialkylborane into borinic ester species, which

then act as extra initiators or chain transfer agents, leading to an increased number of growing chains and broadened molar mass distribution. Et₃B is superior to the longer-alkyl analogy because of its lower activity towards this side reaction. When OPA and epoxide are added in equal molar amounts, both monomers can be fully consumed, despite the side reaction, to generate an alternating-rich acetal-ether copolymer with epoxide-epoxide linkages as the minor components. When epoxide is added to a large excess of OPA, the product becomes a func-

tional polyether with acetal groups enriched in the central part of the backbone. This is attributed to the exceedingly high reaction activity of OPA towards alkoxide species, as demonstrated by DFT calculations. In both cases, the products were readily degradable through acetal hydrolysis under acidic (HCl) conditions. In particular, acetal-functionalized polyethers can break selectively in the middle of the chain, which is highly useful for improving the degradability and recyclability of polyether-PU.

Conflict of Interests

The authors declare no interest conflict.



Electronic Supplementary Information

Electronic supplementary information (ESI) is available free of charge in the online version of this article at <http://doi.org/10.1007/s10118-025-3297-7>.

Data Availability Statement

The data that support the findings of this study are available from the corresponding author upon reasonable request. The authors' contact information: msjpzhao@scut.edu.cn (J. Z.).

ACKNOWLEDGMENTS

This work was financially supported by the National Key R&D Program of China (No. 2022YFC2805103), the National Natural Science Foundation of China (Nos. 52022031 and 52263001), and the Foundation from Qinghai Science and Technology Department (No. 2022-ZJ-944Q).

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